Laboratory of Organic Unit Reactions (Special Issue on the Commemoration of the Fiftieth Anniversary)

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LABORATORY OF ORGANIC UNIT REACTIONS

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The Laboratory was succeeded by Prof. S. Oka in 1973 after the former Head Prof. S. Kunichika's retirement. Studies on reactivities of unsaturated hydrocarbons carried out under the supervision of Dr. Kunichika not only succeeded in exploitation of a new synthetic method for methylmetacrylate from propylene but also brought many fundamental achievements concerning to various organic reactions, especially to those catalyzed by transition metals. Then the research interest has been directed to organotransition metal chemistry from both preparative and mechanistic viewpoints. The research field also has been spread over organic sulfur chemistry and bioorganic chemistry since Associate Prof. Dr. A. Ohno joined the group in 1974.

Some of main progresses in the last decade will be summarized.

I. Studies on Reactivities of Unsaturated Hydrocarbons and Their Derivatives

1. Synthesis of Methylacetylene by Pyrolysis of Propylene

The following results were added to those obtained before 1966. Addition of a small amount of iodine not only accelerated pyrolysis of propylene remarkably but also was effective for syntheses of methylacetylene and allene. Zero conversion method was used to identify the main primary and secondary products. A free radical chain mechanism has been proposed for the main reactions.

2. Carboxylation with Nickel Catalysts

Carboxylation of methylacetylene which has lower reactivity than that of acetylene was investigated. Methyl methacrylate was obtained in satisfactorily high yields with nickel carbonyl catalyst under appropriate reaction conditions. Allene and propylene were also carboxylated successfully to methyl methacrylate and methyl isobutyrate, respectively.

II. Studies on Reactions Catalyzed by Transition Metals

1. Reactions of Allene with Palladium

In the course of the study on transition-metal-catalyzed reactions, it was realized that a study on elementary reactions in organometallic chemistry is necessary for a better understanding of metal-catalyzed reactions and also for a design of suitable catalysts. Allene is particularly suitable for this purpose because it gives stable η^3-allyl complexes by the reaction with transition metals. Using palladium as the metal component, some chemistry of insertion reaction was examined. Reaction of allene with palladium (II) salts gives η^3-allyl complexes and/or 2-allyl-η^3-allyl com-

plexes depending on the reaction conditions. This observation was shown to be explained by the concept of insertion promoted by a π-acid. Another driving force for the insertion, the release of strain in a substrate complex, was demonstrated for the reaction of allene with 2,2′-bi-(η^3-allyl)-dipalladium complexes. A new binuclear palladium complex of allene trimer ligand was isolated, which could be regarded as a model compound for polymerization of allene.

2. Cyanation of Aryl Halides Catalyzed by Palladium

The displacement reaction of various non-activated aryl halides with cyanide ion was investigated in the presence of palladium salts. Various aryl iodides and bromides were converted into the corresponding aryl cyanides almost quantitatively. Detailed examination on the catalyst, co-catalyst, solvent, and reaction condition showed that the reduced palladium species may be the active catalyst. The reaction is more useful for the syntheses of aryl cyanides than the conventional Rosenmund-von Braun reaction.

3. Palladium-Catalyzed Decomposition of Azides to Nitriles

Palladium metal has been found to catalyze the decomposition of benzyl azide to give benzonitrile, benzylamine, and N-benzylidenebenzylamine. The presence of a suitable hydrogen acceptor such as diphenylacetylene improved the yield of benzonitrile at the sacrifice of benzylamine, whereas the yield of N-benzylidenebenzylamine remained constant. The reaction was shown to be applicable to the preparation of some other nitriles including aliphatic ones. The present procedure provides a method to obtain various nitriles without elongating the skeletal carbon chain of the starting halides.

III. Studies on Abnormal Substitution of Aromatic Compounds

Halogenation of Aromatic Hydrocarbons by Metal Halides

Aluminium chloride and some other metal chlorides have been found to act as chlorinating agents for anthracene, in the presence of catalytic amount of nitrogen dioxide under an atomosphere of oxygen, giving mono- or di-chloroanthracene in satisfactorily high yields. This is the first example in which aromatic ring was oxidatively chlorinated with halides of metals that cannot change the valency. It was clarified that nitrogen dioxide is essential to the reaction and oxygen serves to reproduce nitrogen dioxide from the corresponding reduced species. The scope and the mechanism of this new reaction are under investigation.

IV. Studies on Biomimetic Reactions

1. Reaction of NAD(P)H Model Compounds

In order to elucidate the mechanism of biological reductions with NAD(P)H–dependent dehydrogenases and to extend the reaction into organic syntheses, biomimetic reductions with NAD(P)H model compounds have been studied. A mechanism in which one-electron transfer is followed by successive transfers of a proton

and an electron from NAD(P)H or its models to a substrate was proposed and, based on the proposed mechanism, biomimetic respiratory chain coupled with an oxidative phosphorilation of ADP was constracted. Biomimetic asymmetric reductions were also achieved by using chiral model compounds. Some metal ions were found to catalyze the reduction as well as asymmetric induction and the role of these metal ions, or mimetic enzymes, are now being investigated.

2. Model Reactions of Biotin

It was found that intramolecular C→N and N→C migrations of acyl or alkoxycarbonyl groups take place quite easily in some derivatives of 2-methylthiobenzimidazole under mild conditions. The mechanism was studied and the result was discussed in relation to the mechanism of biological biotin-dependent carboxylation. Namely, was suggested the possibility of N-carboxylated biotin to be a biologically active species.

V. Studies on the Chemistry of Thiocarbonyl Compounds

Reactions of thiocarbonyl compounds, mainly of thioketones, were investigated. It was found that a charge-transfer complex is involved as an intermediate of the reaction of thioketone with a nucleophile. Physico-chemical properties of thiocarbonyl group was also studied in relation to those of carbonyl groups. Thioketones were also subjected to photochemical reactions.

Publications

(* indicates an article published in Japanese)

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Reviews

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